

November 10, 1965
Washington, D.C.

THE GEORGE WASHINGTON UNIVERSITY
PRINCIPAL INVESTIGATOR: DR. N. FILIPESCU

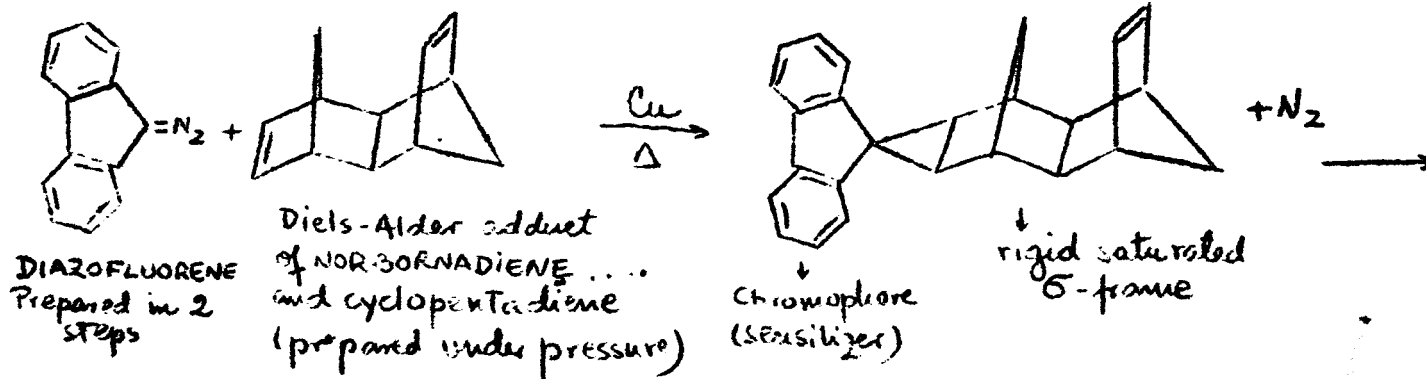
SEMI-ANNUAL RESEARCH REPORT ON GRANT SC-NsG-603
ORGANIC SYSTEMS INVOLVING TRANSITION METALS FOR
OPTICAL MASER MATERIALS

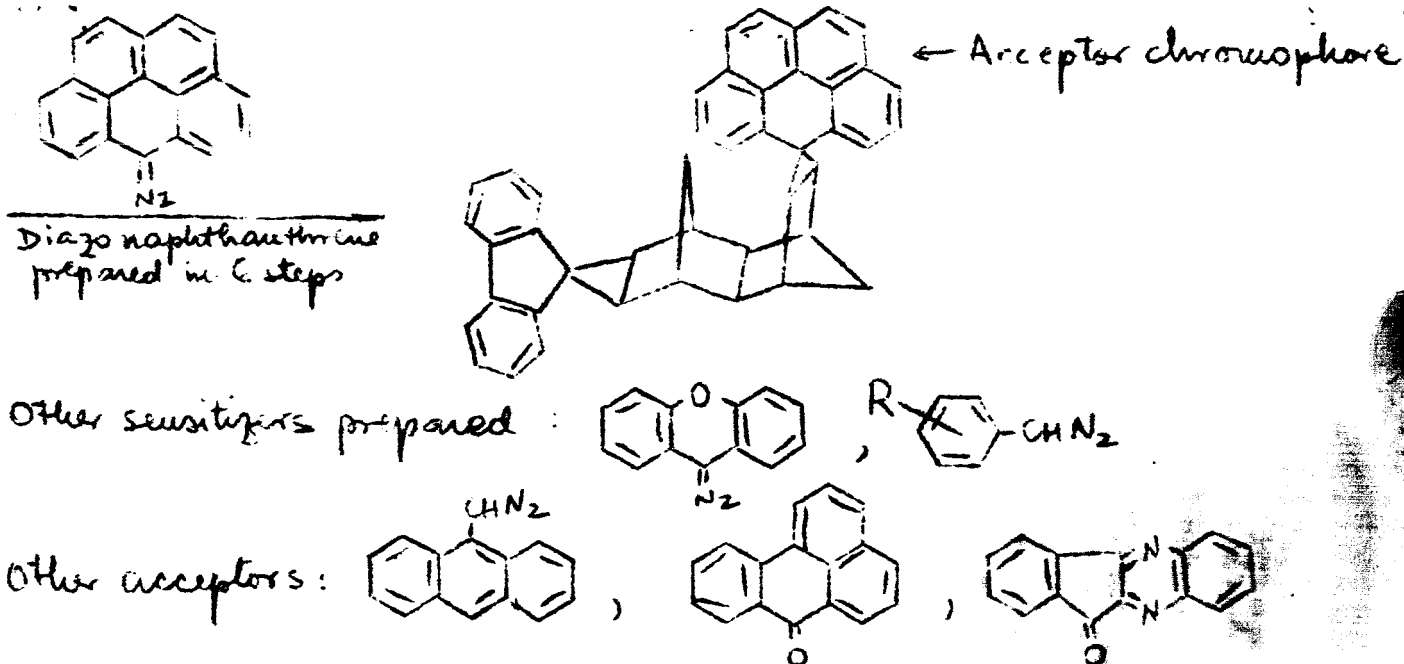
During the period 1 April to September 30, 1965 progress has been in this work along the following directions:

- (1) Synthesis, purification and identification of new compounds.
- (2) Spectroscopic measurements (absorption, fluorescence, phosphorescence, lifetime, quantum efficiency)
- (3) Solvent effects on the spectral characteristics
- (4) Sensitized fluorescence in systems involving intermolecular transfer of energy from an organic sensitizer to rare earth ions in solution.
- (5) Analysis and interpretation of spectral data
- (6) Theoretical work regarding: (a) intramolecular transfer of electronic energy between organic chromophores, (b) comparison of experimental observations with theoretical predictions, (c) correlation of spectral data to molecular structure.
- (7) The work on "Intramolecular Energy Transfer in Homogeneous and Mixed Organic Complexes of Rare Earth Ions" has been submitted for publication and a copy of the manuscript is attached to the report.

(1) Synthesis, purification and identification. New complexing organic agents and lanthanide chelates have been prepared. Experimental conditions have been established to obtain both the free ligand and rare earth chelates from: benzoyl-trifluoroacetone, di-2-naphthoylethane, 2-naphthoylethane, α, α' -dipyridyl, 1,10-phenanthroline. Purification has been accomplished by repeated recrystallization from appropriate solvents. The Europium chelates were used for spectroscopic determinations - which will continue - and will be tested as laser materials.

Model compounds for intramolecular electronic energy transfer between organic chromophores have been selected and synthetic work is in progress. The first phase in this direction will involve the verification of Förster's Theory with respect to the dependence of transfer efficiency on the distance between the chromophores and their mutual orientation. Rigid molecules have been selected as model compounds to avoid free rotation which will lead to undetermined orientation and distance. Here are some examples:





Details of synthesis of these and other selected model compounds will be given when a manuscript will be submitted for publication.

(2) Spectroscopic Measurements. Experimental description and examples of spectra determined are outlined in the attached manuscript. The fluorescence spectra measured for the microcrystalline Eu homogeneous and mixed chelates (see footnote 19) are the best published emission spectra, characterized by very high resolution.

Measurement of quantum efficiency of about 30 Eu chelates in different solvents is almost completed. Work of very high accuracy is required in these determinations.

(3) Solvent effects. The previous manuscript entitled "Solvent and Temperature Effects on Fluorescence Emission of Eu B-Diketonates" was accepted for publication in the Journal of Inorganic and Nuclear Chemistry" and will be published in December 1965 or January 1966. Reprints will be sent to NASA.

Solvents in which the quantum efficiency of the better performing chelate laser materials is superior to those used presently have been found. This in turn should lead to liquid lasers of higher efficiency.

(4) The Study of Sensitized (collisional) fluorescence using organic sensitizers in solution of ionic rare earth salts is quite advanced at present. Here are some essential findings:

- (a) The transfer of energy from the absorbing organic sensitizer to the rare earth ion takes place by collision, being a diffusion controlled process.
- (b) The energy transfer takes place from the lowest excited triplet of the sensitizer (sensitivity to oxygen, energetic location of the triplet)

- (c) The maximum in the excitation spectrum coincides with the absorption of the sensitizers containing a heteroatom suggesting a localized site in the $\pi \rightarrow \pi^*$ lowest triplet for most efficient sensitization of the rare earth ion.
- (d) The quantum efficiency for sensitized rare earth ion fluorescence is comparable to that of chelates suggesting good potential as laser candidates with the advantage of possible use of larger diameter cavities by concentration control of the sensitizer and Eu ions.
- (e) A large number of sensitizers and solvents have been tested leading to the selection of the most efficient systems for lasers.
- (5) Illustration of spectral interpretation is found in the attached manuscript. The Quantum Theory is used in most theoretical analysis (6) related to the problems under investigation and future publications will be attached to reports to indicate developments in this respect.

During this period the Principal Investigator worked part time, one graduate student (Research Assistant) full time, and other two graduate students (Research Assistants) half-time.

Attached Manuscript

ABSTRACT

The absorption, phosphorescence and phosphorescence excitation spectra of mixed Gd chelates reveal an interaction between the two types of ligand chromophores resulting in partial energy transfer from one to the other. The relatively small transfer efficiency is explained by the unfavorable orientation of the two chelating groups. In mixed Eu chelates, the ionic fluorescence is excited by light absorbed by either ligand. The fluorescence spectra of the tris, tris-aqua, tetrakis and mixed complexes are discussed in relation to molecular configuration. Preliminary results of the first order Stark effect calculations using distorted electrostatic models agree with the existence of a monomer-dimer mixture in the nominal tris chelates EuT_3 and EuD_3 . This is confirmed by molecular weight determinations. The tetrakis and mixed Eu chelates are present as nonequivalent stereoisomers which explain the number of fluorescence lines observed.

Département of Chemistry, The George Washington University, Washington 6, D. C.
and Goddard Space Flight Center, NASA, Greenbelt, Maryland.

Intramolecular Energy Transfer
in Homogeneous and Mixed Lanthanide Complexes

by: N. Filipescu, N. McAvoy, K. Moorjani¹, S. Bjorklund, C. M. Hurt, and
J. Zumoff

Introduction

Rare earth ions incorporated in organic chelates by coordination through donor atoms such as oxygen or nitrogen, when excited in the region of light absorption associated primarily with the organic ligand, exhibit characteristic intra-4f parity forbidden fluorescence similar to the inorganic single crystal system. Direct excitation of the metal ion is not responsible for the line emission which, instead, is the result of an intramolecular energy transfer from the excited electronic states of the organic complex to the localized 4f energy levels of the chelated ion. The characteristic europium ion emission in homogeneous chelates (i.e., one ligand) has been previously investigated for both tris and tetrakis β -diketonates^{2,3} and dipyriddy complexes.⁴

We have reported^{2a,b} on the effect of substituents attached directly to the β -diketonate chelate ring or more distant substituents on the electronic states

-
- (1) Department of Physics, Catholic University, Washington, D. C.
(2) (a) N. Filipescu, W. F. Sager, and F. A. Serafin, J. Phys. Chem. 68, 3324 (1964); (b) *ibid.* 69, 1092 (1965); (c) N. McAvoy, N. Filipescu, M. R. Kagan, and F. A. Serafin, J. Phys. Chem. Solids 25, 461 (1964)
(3) (a) L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris J. Am. Chem. Soc. 86, 5117 (1964); (b) H. Bauer, J. Blanc, and D. L. Ross, *ibid.* 86, 5125 (1964); (c) M. L. Bhaumik et. al., J. Phys. Chem. 68, 1490 (1964); (d) C. Brecher, H. Samelson, and A. Lempicki, J. Chem. Phys. 42, 1081 (1965); (e) J. J. Freeman and G.A. Crosby, J. Phys. Chem., 67, 2717 (1963)
(4) (a) S. P. Sinha, Spectrochim. Acta 20, 879 (1964); (b) *ibid.* J. Inorg. Nucl. Chem. (1965, in press)

of the organic ligand and the overall intramolecular energy migration in rare earth β -diketonates. The splitting of the lines and distribution of fluorescence among individual transitions originating at the 5D_0 and 5D_1 levels and terminating at the 7F ground multiplet of europium ion were found to be highly sensitive to changes in the organic part of the molecule. Both the symmetry and the intensity of the molecular field about the Eu^{3+} ion were significantly affected by modifications in ligand and consequently the transition probabilities inside the 4f shell are directly affected.

The present work is concerned with the energy migration processes in Eu and Gd complexes which have either only one type of ligand surrounding the lanthanide ion or two different chelating groups. Compared to a homogeneous chelate, a mixed system involves two sets of organic electronic excited states associated with the two different ligand chromophores and a more complex and asymmetric electric field about the rare earth ion induced by the surrounding atoms. This system has its own characteristics and is expected to be quite different from the one type ligand chelates. The two organic chromophores can be selected such that their absorption maxima are at different wavelengths and excited separately. The two ligands may interact with each other and with the europium ion to modify the overall intramolecular energy migration.

Experimental

Materials - Methods previously described²⁻⁴ have been employed to synthesize the following complexes: Tris chelates: Eu tris(theonyltrifluoroacetate) (EuT_3), Eu tris(dibenzoylmethide) (EuD_3), Eu tris(benzoylacetonate) (EuB_3);

Tetrakis chelates: Eu tetrakis(theonyltrifluoroacetate)piperidinium (EuT_4P), Eu tetrakis(dibenzoylmethide)piperidinium (EuD_4P), Eu tetrakis(benzoylacetonate)piperidinium (EuB_4P); Bis chelates: Eu bis(dipyridyl) $\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (EuDipy), Eu bis(1,10-phenanthroline) $\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (EuPhen); Tris-aqua chelates: Eu tris(theonyltrifluoroacetate)aqua (EuT_3A), Eu tris(dibenzoylmethide)aqua (EuD_3A), Eu tris(benzoylacetonate)aqua (EuB_3A); Mixed chelates: Eu tris(theonyltrifluoroacetate)dipyridyl (EuT_3Dipy), Eu tris(theonyltrifluoroacetate)phenanthroline (EuT_3Phen), Eu tris(dibenzoylmethide)dipyridyl (EuD_3Dipy), Eu tris(dibenzoylmethide)phenanthroline (EuD_3Phen), Eu tris(benzoylacetonate)dipyridyl (EuB_3Dipy), Eu tris(benzoylacetonate)phenanthroline (EuB_3Phen); Gd chelates: Gd tris(theonyltrifluoroacetate) (GdT_3), Gd tris(theonyltrifluoroacetate)aqua (GdT_3A), Gd tris(theonyltrifluoroacetate)dipyridyl (GdT_3Dipy), Gd tris(theonyltrifluoroacetate)phenanthroline (GdT_3Phen).

The tris β -diketonates aqua were prepared in $\text{EtOH-H}_2\text{O}$ from EuCl_3 , β -diketone and NaOH^{3a} . The tris compounds were obtained on heating the tris aqua chelates for 48 hours at 110°C in vacuum. The tetrakis β -diketonates were prepared in absolute EtOH adding piperidine to 4:1 mixture of ligand and EuCl_3 . The procedures described by Melby et. al.^{3a} and Bauer et. al.^{3b} were employed for the preparation of mixed chelates. The chelates were repeatedly recrystallized from appropriate solvents and dried in vacuum. Analysis^{3d} confirmed their composition.

Absorption Spectra.- Absorption in ultraviolet was determined with a Cary 15 spectrophotometer⁵ in double beam mode at room temperature in methanol. Ionic absorption spectra for Eu^{3+} in chelates were measured with the Cary 14⁵ at room temperature and high concentrations (10^{-1}M) in 10cm path cells in dimethylformamide.

(5) Applied Physics Corporation, Monrovia, California

Fluorescence Spectra.- The fluorescence emission of the complexes was determined in microcrystalline powders at 77°K. Light from a 1000 watt, water cooled high pressure AH6 mercury lamp was filtered through a NiSO_4 water solution and a Corning CS7-54 filter and directed into a metal box constructed to prevent stray light from interfering with the measurements. A quartz dewar was positioned in the box such that the excitation light would be focused on the sample which was sealed between quartz slides and immersed in liquid N_2 in the clear bottom part of the dewar. The fluorescence emission was directed through a Corning CS3-70 filter into the Cary 14 and detected by a R136 red-sensitive photomultiplier. The entrance slit to the Cary was adjusted manually to control the amount of light entering the monochromator. Dry air was caused to circulate inside the box to prevent possible frosting on the dewar and the 90° geometry was rigidly maintained. Spectra were recorded from 7500 to 5000Å and corrected for the different slit widths by extrapolating all the peaks to a common slit width (0.5mm) on relative intensity vs. slit width charts. The charts were determined by varying the slits for individual peaks and recording the output at each slit width. The spectra were also corrected for the spectral response of the photomultiplier tube. The area under the peaks were calculated by considering the peaks as Gaussian structures and multiplying the relative intensities by the line width (in cm^{-1}) at the half power points. The percentage of the total fluorescence was determined for each line. The arithmetic work was done by a 7090 computer.

Organic Emission of Free Ligands and Gd Chelates, Phosphorescence and Fluorescence Excitation Spectra.- Organic fluorescence and phosphorescence of free ligands and Gd chelates were determined at liquid nitrogen temperature in EPA with the Aminco-Bowman spectrophotofluorimeter⁶ employing a 150 watt xenon lamp for excitation and an R-136 photomultiplier as detector. Freshly prepared samples were poured in the quartz tube and immersed in liquid nitrogen in the dewar supplied with the phosphoroscope attachment. The rotating shutter was not used to detect the feeble organic fluorescence. The phosphorescence excitation spectra were measured using the same arrangement but scanning the excitation monochromator. The fluorescence excitation spectra (of Eu chelates) were run similarly, only the chelates were dissolved in dimethylformamide in a square 1 cm. cell in 90° geometry at room temperature. For these measurements, the concentrations used were such that the amount of light absorbed before the center of the 1cm. cell would be less than 4.5% of the light at the wavelength of maximum absorption. No correction was needed, therefore, for the inner filter absorption by the solution. Both phosphorescence excitation and fluorescence excitation spectra were corrected for the spectral output of the Xe lamp and the corresponding spectral dispersion at various wavelengths for the slit widths employed.⁷ The decay times of the organic phosphorescence were measured at 77°K in EPA using the time base recorder supplied by the manufacturer.⁶

Lifetime Measurements - The excitation source employed was a "strobotac" Type 1531-A electronic stroboscope⁸ with a flash duration of approximately three microseconds. The light was focused into a black box after passing through a

(6) American Instrument Co., Silver Spring, Maryland

(7) (a) C. A. Parker et. al., Analyst 82, 606 (1957); (b) ibid., 85, 587 (1960);

(c) ibid., Anal. Chem. 34, 502 (1960)

(8) General Radio Company, West Concord, Mass.

Corning CS7-60 filter. The dewar-sample arrangement was similar to fluorescence measurements. The fluorescence was directed through a Corning CS3-66 filter into a grating monochromator⁹ at right angle to the excitation beam. The slits were adjusted to provide maximum resolution, and the detector used was an RCA 7265 S-20 photomultiplier. The photomultiplier signal was displayed on a Type 535A oscilloscope.¹⁰

RESULTS

In Figure 1 the absorption spectra of three different Eu chelates are compared to those of the free ligands. Changes taking place in the chelating agent absorption upon complex formation can be compared for the tris (EuT_3), tetrakis (EuT_4P), and mixed EuT_4Dipy chelates. A mixture of Dipy and T in a 1:3 ratio does not show any interaction between the two free ligands, the spectra of the mixture being a perfect addition of the separate individual absorbances. There is very little difference between the absorption spectra of Dipy (10^{-5}M) and $\text{Eu}(\text{Dipy})_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ ($0.5 \times 10^{-5}\text{M}$) manifested in a slight bathochromic shift on complex formation of about 30\AA for all three peaks and an insignificant increase in absorbance. A different picture is presented by the absorption of EuT_4P (10^{-5}M) when compared with the free ligand T ($4 \times 10^{-5}\text{M}$). On chelate formation, the first $\pi \rightarrow \pi^*$ band at 3375\AA increases markedly. This could be simply the result of complete conversion of the ketone-enol equilibrium in the free ligand to enolate anion in the chelate. There is ample evidence that aromatic β -diketones in solution are largely enolic and that the keto-enol equilibrium depends on the solvent polarity.¹¹ However, the presence of the CF_3 group on T increases the

(9) Bausch and Lomb Optical Company, Rochester, N. Y.

(10) Tektronix, Inc., Portland Oregon

(11) (a) F. Arndt, L. Loewe, and R. Ginkok, Rev. Faculte Sci. Univ. Istanbul Ser. A, 11, No. 4, 147 (1964); (b) G. S. Hammond, W. G. Borduin, and G. S. Guter, J. Am. Chem. Soc. 81, 4682 (1959); (c) J. C. Reid and M. Calvin, J. Am. Chem. Soc., 72, 2948 (1950)

amount of ketone by lack of possible conjugation and negative inductive effects.^{11c}
The hyperchromism of the absorption band centered at 3425Å in dibenzoylmethane on chelate formation is much less significant than for theonyltrifluoroacetone because the first is essentially enolic in solution.

The absorption spectrum of the mixed chelate EuT_3Dipy is quite different from an equivalent mixture of free ligands. The main $\pi \rightarrow \pi^*$ band is red shifted about 40Å and intensified to double the value of ϵ , whereas an opposite hypochromic effect is observed in the 2000-3500Å range associated with absorption by the Dipy chromophore and $S \rightarrow S''$ in T. These differences indicate that some intramolecular coupling between the two ligand chromophores takes place in the mixed chelate. In addition, in mixed chelates the presence of the heavy and paramagnetic rare earth ion affects the interaction between the two ligand chromophores by changing the character and lifetime of their electronic levels.^{2a, 12} These phenomena are best investigated in Gd chelates by measuring the phosphorescence of the system in the absence of Eu^{3+} chromophore. The results can be extended to the Eu complexes without any appreciable error because of the close atomic weight and paramagnetic characteristics of the two neighboring rare earth elements.

The emission and phosphorescence excitation spectra of three free ligands and their Gd chelates in rigid matrix at 77°K are shown in Figures 2 to 5, and the phosphorescence lifetimes are given in Table 1. A very weak organic fluorescence is observed in both free ligands and their Gd chelates, the values of $\phi_p/(\phi_p + \phi_f)$ being 0.96 for T and GdT_3 , 0.86 for Dipy, and 0.88 for Phen

-
- (12) (a) P. Yuster and S. I. Weissman, J. Chem. Phys. 17, 1182 (1949);
(b) N. Christodouleas and S. P. McGlynn, J. Chem. Phys., 40, 166 (1964);
(c) K. B. Eisenthal and M. A. El-Sayed, J. Chem. Phys., 42, 794 (1965);
(d) H. Tsubomura and R. S. Mulliken, J. Am. Chem. Soc., 82, 5966 (1960).

respectively. No apparent change in $\phi_p/(\phi_p + \phi_f)$ occurs on complex formation. However, the phosphorescence decay times of the free ligands are modified drastically due to changes in both radiative and radiationless $T_1 \rightarrow S_0$ transition probability by the presence of the heavy and paramagnetic Gd ion.¹²

This effect is essentially an enhanced spin-orbit admixing of the $T_1 \rightarrow S_0$ into the $S_1 \rightarrow S_0$ transition upon complexation with Gd³⁺ for T and Phen ligands and an

Table 1. Phosphorescence lifetimes of free ligands and Gd chelates in EPA at 77°K

Ligand	Free Ligand			GdT ₃			GdT ₃ Dipy			GdT ₃ Phen		
	$\lambda_{\text{exit.}}$	$\lambda_{\text{em.}}$	Sec.	$\lambda_{\text{exit.}}$	$\lambda_{\text{em.}}$	Sec.	$\lambda_{\text{exit.}}$	$\lambda_{\text{em.}}$	Sec.	$\lambda_{\text{exit.}}$	$\lambda_{\text{em.}}$	Sec.
	m μ	m μ		m μ	m μ		m μ	m μ		m μ	m μ	
T	340	493	1.0	340	493	0.75	340 280	493 520	0.75 0.85	344	524	0.5
Dipy	285	448	0.7	-	-	-	280 235	456 426	2.4 5.0	-	-	-
Phen	265	450	3.5	-	-	-	-	-	-	280	420	0.55

opposite decrease in admixture for Dipy inherent to its flexible structure. In general, the decay of the phosphorescence was found to be exponential; however, for Dipy the lifetime is a function of wavelength being shorter at longer wavelengths, which is not unusual.¹³

The corrected^{7,14} phosphorescence excitation spectra for the free ligands and GdT₃, displayed in Figure 2, are nearly proportional to the corresponding absorption spectra. This result is consistent with a constant quantum yield of

(13) R. Bersohn and I. Isenberg, J. Chem. Phys., 40, 3175 (1964)

(14) The apparent excitation spectra were corrected for the variation in intensity of the exciting Xe lamp at different wavelengths. For details see C. E. White, M. Ho, and E. Q. Weimer, Anal. Chem. 32, 438 (1960)

emission anywhere in the absorption band. The analysis of the excitation and phosphorescence spectra of the mixed chelates in Figure 2 obtained by selective excitation and by isolating phosphorescence bands characteristic to one individual ligand-chromophore revealed the presence of intramolecular energy migration from one ligand to another. Thus phosphorescence from T is observed on excitation with light absorbed essentially by Dipy ($234 \text{ m}\mu$) or Phen ($229 \text{ m}\mu$) in GdT_3Dipy and GdT_3Phen respectively. Conversely, the characteristic Dipy phosphorescence ($458 \text{ m}\mu$) can be excited at wavelengths absorbed exclusively by T ($335 \text{ m}\mu$) in GdT_3Dipy , and Phen phosphorescence ($457 \text{ m}\mu$) is excited at $335 \text{ m}\mu$ in GdT_3Phen .

This process can take place by either dipole-dipole resonance or by exciton transfer, the overlap requirement of donor emission and acceptor absorption being satisfied for the singlet-singlet transfer from Dipy or Phen to T. At the same time, the overlap of the lowest triplets and their vibrationally excited states makes mutual triplet-triplet resonance transfer operational. Additional experiments proved that no similar energy migration takes place in mixtures of free ligands¹⁵ in which the two chromophores are situated more than 100\AA apart. The observed energy transfer from one ligand to another in

(15) Solutions of $\text{T}(3 \times 10^{-5}\text{M}) + \text{Dipy}(10^{-5}\text{M})$ in EPA, and $\text{T}(3 \times 10^{-5}\text{M}) + \text{Phen}(10^{-5}\text{M})$ in EPA. The two ligands did not show any association in solution, their absorption spectra being rigorously additional.

mixed chelates, although clearly shown in both excitation and phosphorescence spectra, has a smaller efficiency compared to other systems exhibiting this phenomenon.¹⁶ This can be explained from the geometrical arrangement of the two chromophores in mixed chelates. Dipy (or Phen) in GdT_3 Dipy (or GdT_3 Phen) is situated in a plane that forms a 90° angle with the planes of two adjacent T groups and essentially in the same plane as the third (opposing) T groups, or simply at right angles with each of the three T groups.¹⁷ Therefore, the orientation factor K^{18} , being a function of the cosine of the angle between the donor and acceptor transition dipoles, has a very small value.

(Next page)

-
- (16) (a) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, J. Am. Chem. Soc., 87, 2322 (1965); (b) O. Schnepp and M. Levi, *ibid.* 84, 172 (1962); (c) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, 87, 995 (1965)
- (17) Two possible stereoisomers: the dodecahedron and the Archimedean antiprism (see discussion, Models D and E respectively). Only the enolate ring of theonyltrifluoroacetate anion is taken into consideration because the possible stereoisomers with different arrangement of the CF_3 and thienyl groups will be identical in enolate chromophore orientation.
- (18) (a) Th. Forster, Radiation Res. Suppl. 2, 326 (1960); (b) *ibid.*, Discuss, Faraday Soc. 27, 7 (1959)

Replacing Gd with Eu in mixed chelates, the system becomes more complex containing three interacting chromophores. The corrected fluorescence (Eu^{3+}) excitation spectrum in mixed chelates in solution parallels closely the absorption spectrum proving that energy absorbed by either ligand is transferred to the complexed ion. The characteristic Eu fluorescence of the different complexes studied obtained on excitation with light absorbed by the organic part, is shown in Figures 7 to 23¹⁹. In most previous work on Eu chelates^{2,3}, the 6300 to 7500 Å spectral range corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition has been neglected. Presently, we include these lines in the emission spectra of tris, tris-aqua, and tetrakis, diketonates as well as Dipy, Phen, and mixed Eu chelates.

The fluorescence spectra were examined in microcrystalline powders to avoid the partial dissociation and additional coordination which take place on solvation.^{3d,20} Both ionic absorption (Figure 6) and emission have been employed to identify transitions from $^5\text{D}_0$ and $^5\text{D}_1$ levels to the ground ^7F multiplet. The absorption spectrum at room temperature indicates that the $^7\text{F}_1$ and $^7\text{F}_2$ levels are sufficiently populated to cause absorption lines originating at these levels, which has also been reported by other investigators.²¹ This data provided additional information to help identify the energetic location of the different energy levels and their splitting.

- (19) Figures 7 to 10 are illustrated in the paper. The entire collection of fluorescence spectra (17 diagrams) has been deposited as Doc. No. 8619 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D.C. A copy may be secured by citing the Document Number and by remitting \$2.50 for photoprints or \$1.75 for microfilm in advance payment by check or money order payable to: Chief, Photoduplication Service, Library of Congress.
- (20) N. Filipescu and N. McAvoy, J. Inorg. Nucl. Chem. (in press).
- (21) (a) H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, J. Chem. Phys., 40, 2547 (1964); (b) J. A. Konigstein, 136, A717 (1964)

(Figures 7, 8, and 9)

(Figure 6)

Lifetime measurements of isolated fluorescence lines, expected to help in detailed recognition of the individual lines, were not very conclusive because of the very short life time of the 5D_1 level, comparable to the flash duration of our lamp, the weakness of certain lines and the limited resolution of the monochromator used. The observed groups of lines can be associated with certain transitions in the Eu ion: $^5D_0 \rightarrow ^7F_4$ appears in the 7200 - 6650 Å region, $^5D_0 \rightarrow ^7F_3$ in 6650 - 6440 Å, $^5D_0 \rightarrow ^7F_2$ in 6440 - 6030, $^5D_0 \rightarrow ^7F_1$ in 6030 - 5830 Å, $^5D_0 \rightarrow ^7F_0$ around 5800 Å, and $^5D_1 \rightarrow ^7F_1$ overlap with the organic phosphorescence in the 5700 - 5200 Å region. These assignments are consistent with previous designations^{3d,e}. The number of components observed for various identified levels apparently indicates that the symmetry of the tris-chelates is lower than octahedral and for the tetrakis and mixed chelates lower than tetragonal. (See Discussion, however.)

The relative intensities of the individual fluorescence lines expressed as percentage of total Eu ion emission are listed in Table II. To calculate these values, the fluorescence spectra were corrected for slit width and photomultiplier response (see Experimental). The arrows employed for the $^5D_0 \rightarrow ^7F_4$, $^5D_0 \rightarrow ^7F_3$ and $^5D_1 \rightarrow ^7F_2$ transitions designate "band with structure" with approximate limits at the top and bottom of the group. Only ω_{\max} of clearly defined peaks is given²². This type of characterization was not needed for the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions which give relatively clear sets of lines. The variation in relative intensity of specific transitions on changing the organic part of the chelate molecule is impressive. Some general observations

(22) We found it to be misleading to attempt to identify weak shoulders at the noise level especially for the $^5D_0 \rightarrow ^7F_4$ and $^5D_0 \rightarrow ^7F_3$ transitions in which the number of Stark components is relatively large and the fairly weak lines overlap extensively.

can be made. The tris and the trisqua complexes in each of the three β -diketonates investigated are fairly close in fluorescence distribution among specific $^5D \rightarrow ^7F$ transitions. The relative intensity of the $^5D_0 \rightarrow ^7F_4$ group of lines is highest for the dibenzoylmethides, lowest for benzoylacetonates and intermediate for theonyltrifluoroacetonates. On going from a tris to a tetrakis β -diketonate the effects vary from one type of ligand to another. In EuT_4P the $^5D_0 \rightarrow ^7F_4$ transition remains about the same, whereas the $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_1$ groups increase substantially at the expense of the $^5D_0 \rightarrow ^7F_2$ lines. EuD_4P exhibits an opposite trend: higher intensity for the $^5D_0 \rightarrow ^7F_4$ group and decreased relative contribution from $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_1$. In EuB_4P a sizable decrease in relative intensity is observed for the $^5D_0 \rightarrow ^7F_2$ lines with corresponding increase in the $^5D_0 \rightarrow ^7F_4$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_1$ groups. The formation of mixed diketonates with Dipy or Phen also determines significant changes in relative distribution. Compared to EuT_3 , the mixed EuT_3Dipy and EuT_3Phen complexes show marked increase in the $^5D_0 \rightarrow ^7F_4$ lines at the expense of the $^5D_0 \rightarrow ^7F_2$. On the contrary EuD_3Dipy and EuD_3Phen exhibit enhanced $^5D_0 \rightarrow ^7F_2$ contribution with weakening of the $^5D_0 \rightarrow ^7F_4$ group (compared to EuD_3). The effects on EuB_3 are opposite for EuB_3Dipy and EuB_3Phen . The relative intensities of the $^5D_0 \rightarrow ^7F_4$ and $^5D_0 \rightarrow ^7F_2$ lines in EuDipy and EuPhen are completely reversed. One could extend this discussion to statistical weight of individual lines inside a certain $^5D \rightarrow ^7F$ group. However, at the present time, these are merely observations and no prediction can be made with respect to energy distribution among individual transitions as function of molecular structure or nature of ligands.

The relative (total) fluorescence intensities of different microcrystalline Eu chelates at 77°K are compared in Table III. These figures represent the sum of the areas under all fluorescence peaks after correction for slit width and detector response, on a wave number chart, normalized arbitrarily for $\text{EuT}_3 = 0.2$. Assuming that all chelates absorb about the same number of quanta in the experimental arrangement used, the numbers in Table III should be approximately proportional to the absolute quantum efficiency, which is not known for chelates in powders.

Table III. Relative quantum efficiencies of Eu chelates (powders) at 77°K.

EuT_3	0.20	EuT_3A	0.28	EuT_4P	0.42	EuT_3Dipy	0.90	EuT_3Phen	0.48
EuD_3	0.60	EuD_3A	0.27	EuD_4P	0.43	EuD_3Dipy	0.38	EuD_3Phen	0.29
EuB_3	0.31	EuB_3A	0.13	EuB_4P	0.15	EuB_3Dipy	0.27	EuB_4Phen	0.10
						EuDipy	0.42	EuPhen	0.23

Chelates containing phenanthroline are consistently poorer emitters than their dipyridyl analogs. The variation in relative quantum efficiency does not follow a regular pattern for the three different β -diketonates. This is not unexpected because the presence of different species (stereoisomers or monomer-dimer mixtures), the intersystemcrossing, and the ligand $\rightarrow \text{Eu}^{3+}$ transfer efficiency are all dependent on the substituents attached to the enolate ring. The data obtained in powders cannot be extrapolated to solutions where dissociation, additional coordination, and solvent quenching will be present.

DISCUSSION

The amount of molecular field splitting observed in chelates seems to be markedly higher than in ionic crystals (LaCl_3 , ethyl sulfate, etc.). This implies that the field seen by the rare earth ion is stronger in chelate than in ionic crystals. Since the field strength depends on both the charge and the distance of the surrounding atoms from the rare earth ion, one conjectures that the nearest neighbors are closer in chelates, which is consistent with the partial covalent character of the Eu-O bond.

At least half of the complexes examined exhibited more than five components for the $^5D_0 \rightarrow ^7F_2$ transition, which is the maximum splitting of a level with $J = 2$ in a field of any symmetry. This is a clear indication that more than one emitting species is present. It has been suggested for the tetrakis diketonates^{3d} that dissociation takes place in solution, where EuKe_4^- is in equilibrium with EuKe_3 and Ke^- . However, our results indicate that even in the solid microcrystals exhibiting the correct elemental analysis for a homogeneous compound more than one species are present for ^{many} ~~all~~ tris, tetrakis and mixed chelates. One possibility is that we have a mixture of different stereoisomers formed during synthesis which have nonequivalent molecular fields about the Eu ion and therefore the Stark components are found at different wavelengths. Another alternative is the existence of associated chelate molecules in which the enolate groups serve as bridges between two Eu ions. The existence of stereoisomers has been demonstrated for Gd^{3+} and Y^{3+} tris(acetylacetonates) by chromatographic separation of the optically active

enantiomers^{23,24}. X-ray studies have shown that the acetylacetonates of Co^{2+} and Ni^{2+} are tetrameric^{25a} and trimeric^{25b} respectively in crystalline form. In addition, an investigation of the absorption spectra of Eu tris(acetylacetonate) in different solvents has indicated the presence of both monomer and dimer^{25c}. In chelates derived from unsymmetrical β -diketones and in mixed chelates, the number of possible stereoisomers is larger and considering the fact that the field of force responsible for the decomposition of the energy levels extends beyond the immediate neighborhood of the Eu ion^{2a}, the large number of Stark components observed is not to be unexpected.

The monomeric tris-chelates derived from symmetrically substituted β -diketones (model A, ex. EuD_3) can exist in two mirror image stereoisomers (enantiomers). These isomers will rotate the plane of polarized light in opposite directions but spectroscopically they are identical species. The maximum number of Stark components arising in a field of any symmetrical arrangement in Eu fluorescence are 9 for $^5\text{D}_0 \rightarrow ^7\text{F}_4$, 7 for $^5\text{D}_0 \rightarrow ^7\text{F}_3$, 5 for $^5\text{D}_0 \rightarrow ^7\text{F}_2$, 3 for $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and one for $^5\text{D}_0 \rightarrow ^7\text{F}_0$. The numbers of observed lines from crystalline EuD_3 for the same transitions are 9, 14, 5, 4, and 1 respectively. There must be two emitting species to account for these lines. One alternative is that in microcrystals the tris chelate is essentially dimeric

- (23) T. Moeller, J. Inorg. Nucl. Chem., 9, 82 (1959)
 (24) (a) E. Gulyas, Dissertation Abstracts 15, 2004 (1955); (b) R. H. Marshall, Doctoral Dissertation, Univ. of Illinois, 1954; (c) G. R. Kubler, J. Am. Chem. Soc., 74, 3535 (1952)
 (25) (a) F. A. Cotton and R. C. Elder, J. Am. Chem. Soc., 86, 2294 (1964); (b) G. J. Bullen, R. Mason, and P. Pauling, Nature, 189, 291 (1961); (c) S. Freed, S. I. Weissman, and F. E. Fortess, J. Am. Chem. Soc., 63, 1079 (1941).

and therefore can have two nonequivalent stereoisomers B and C. However these two stereoisomers differ only in the mutual orientation of the two pairs of end groups. These are relatively far from each other and therefore the two species will probably be essentially identical spectroscopic species.

Another possibility is that the powder consists of a monomer-dimer mixture. The general way of preparing tris-diketonates is to heat the hydrated form (or the tetrakis) in vacuum. It is very possible that during this step a certain amount of the monomeric tris-complex is converted to dimer, the final product being a monomer-dimer mixture. Molecular weight determinations of nominally tris-chelates confirmed this hypothesis. For example EuT_3 in benzene gave a number-average molecular weight of 1053 which corresponds to 55 molecules of EuT_3 and 45 molecules of Eu_2T_6 in one hundred molecules in solution.²⁶

In Models A, B, and C the six oxygen atoms of the ligand octahedrally surround the rare earth ion which uses bonding d^2sp^3 orbitals formed by hybridization of the $5d_{x^2-y^2}$, $5d_{z^2}$, $6s$, $6p_x$, $6p_y$, and $6p_z$ orbitals. The empty $5d_{xy}$, $5d_{yz}$, and $5d_{xz}$ orbitals remain available for π -bonding with the π -electrons of the ligand (oxygen atoms). The fact that the partially occupied $4f$ orbitals are not involved in bonding is indicated by the discrete structure of both absorption and emission spectra of the chelated ion and their similarity with those of inorganic ionic salts.

The solid tetrakis chelates are monomeric. They exhibit sharp melting points and their molecular weight in solution²⁶ is slightly less than calculated

(26) A more detailed study of molecular weights will be reported in the near future.

proving some dissociation takes place. There are only two possibilities for the ion to accommodate eight coordinating oxygen atoms: (1) a dodecahedral arrangement stable for the use of d^4sp^3 hybrid orbitals (Model D), and (2) an antiprismatic configuration for d^4sp^3 and d^5p^3 (Model E). These two possible stereoisomers do not have equivalent molecular field about the Eu ion and therefore two emitting species exist in the monomer to explain the number of lines observed. In some cases (EuB_3 , EuB_3A , EuB_4P) the spectra can be interpreted as originating from only one species, which may show a preferential dimer formation for EuB_3 during preparation and equivalent stereoisomers for EuB_4P and EuB_3A , or simply a weaker Stark field resulting in small splitting with less possible resolution of the overlapping components.

We have investigated the splitting of the fluorescence lines in Eu β -ketoenolates in terms of a perturbation produced by the electrostatic effect of the ligand field. Preliminary findings are outlined presently and detailed calculations will be reported elsewhere²⁷. First, we have established the complete equivalence between a ligand field having the negative charge delocalized along the enolate anion and a field produced by a point charge distribution of corresponding symmetry with respect to their electrostatic effects on the 4f levels of the rare earth ion. Then we applied the operator equivalent methods developed for crystal field problems by Judd^{28a,b} and Stevens^{28c} in the calculation of the first-order Stark effect. The results indicate that the 7F_1 level should split into two components for Models A, B, and D, and three for

(27) Submitted for publication in J. Chem. Phys.

(28) (a) B. R. Judd, Mol. Phys. 2, 407 (1959); (b) *ibid.*, Proc. Roy. Soc. A 228 120 (1955); (c) K. W. H. Stevens, Proc. Phys. Soc. 65, 209 (1952).

E respectively. In a mixture of A and B, one should observe four different lines for the $^5D_0 \rightarrow ^7F_1$ transition, and in a D and E mixture of tetrakis stereoisomers one should observe five lines. This agrees with the experiment. In light of these calculations, the five components of the 7F_1 level observed in the fluorescence spectrum of EuD_4P can be assigned as belonging to species D (535 and 306 cm^{-1}) and E (448, 361, and 332 cm^{-1}).

The $^5D_0 \rightarrow ^7F_2$ transition should generate 8 components for an A and B (or C) mixture and 9 for a D and E mixture, which we actually observe for EuD_3 and EuD_4P respectively.²⁹ These results enabled us to extract from experimental data the values of the ligand field parameters responsible for the splittings of the 7F_1 and 7F_2 levels, to assign the individual lines to the various stereoisomers, and to reconstruct the equivalent point charge models associated with the isomeric species.

The first Eu chelate found to exhibit laser activity in solution was $\text{EuB}_4\text{P}^{30}$. Subsequently a few more have been added to the list, all belonging to the tetrakis β -diketonate species. It has been puzzling to find out that chelates with equivalent or higher quantum efficiency did not perform as lasers. The lifetime of the 5D_0 state does not vary critically, remaining in the millisecond range for most chelates in solution. But the presence of a unique emitting species, a relatively high quantum efficiency, and a proper fluorescence distribution

-
- (29) Table II indicates only 8 lines for the $^5D_0 \rightarrow ^7F_2$ transition in EuD_4P . Subsequent high-resolution analysis of the fluorescence spectrum has revealed the presence of 9 lines.
- (30) (a) A. Lempicki and H. Samelson, *Phys. Letters*, **4**, 133 (1963); (b) E. J. Schimitschek, *Appl. Phys. Letters* **3**, 117 (1963); (c) M. L. Bhaumik et. al., *J. Phys. Chem.*, **68**, 1490 (1964); (d) A. Lempicki, H. Samelson, and C. Brecher, *J. Chem. Phys.*, **41**, 1214 (1964).

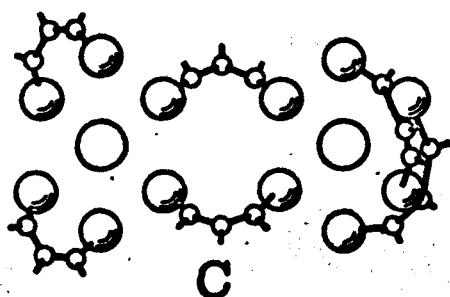
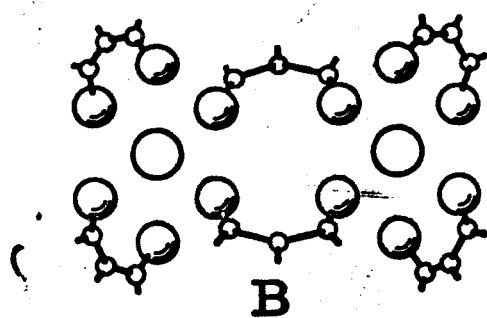
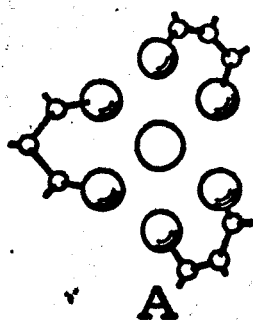
among individual lines are also essential for lasing. The existence of two or more species in solution will lead to undesired competition. Another loss of effective pumping energy is found in transitions originating at the 5D_0 level and terminating at 7F levels other than 7F_2 , and these are by no means insignificant. Both empirical and theoretical correlations of these factors with molecular structure are important in designing the most adequate systems for liquid chelate lasers.

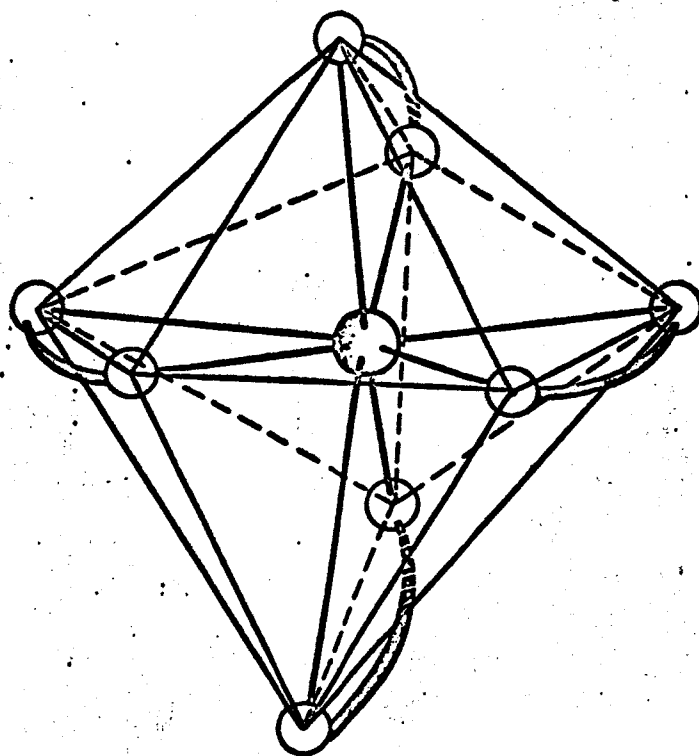
Acknowledgement. Part of this work was carried out under NASA Grant Nsg603.

Table II. Relative Intensities of Individual Fluorescence Lines

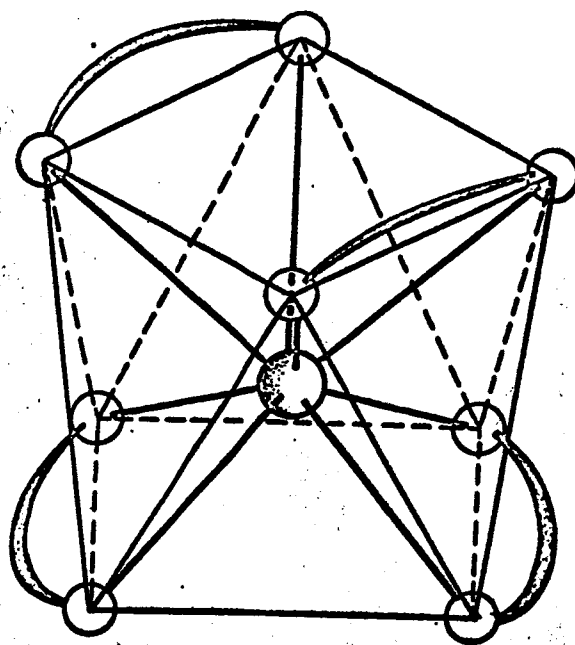
[illegible]

Percentage Total Emission



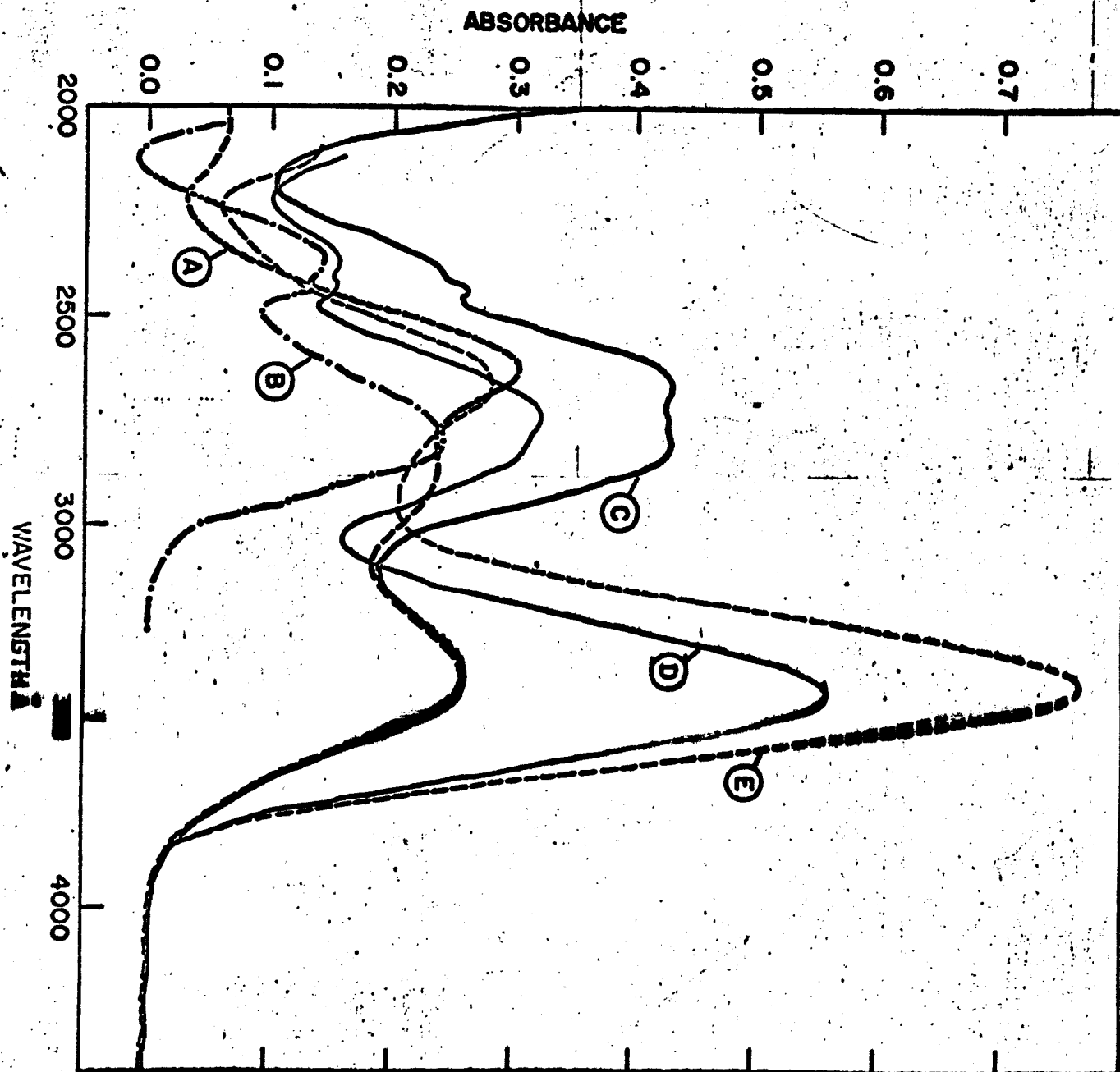


D



E

Figure 1. Absorption spectra of free ligands and their Bi chelates in CH₃OH.
 (A) T 3×10^{-5} M; (B) Dipy 10^{-5} M; (C) T 3×10^{-5} M + Dipy 10^{-5} M;
 (D) BiT₃Dipy 10^{-5} M; (E) BiT₄P 10^{-5} M.



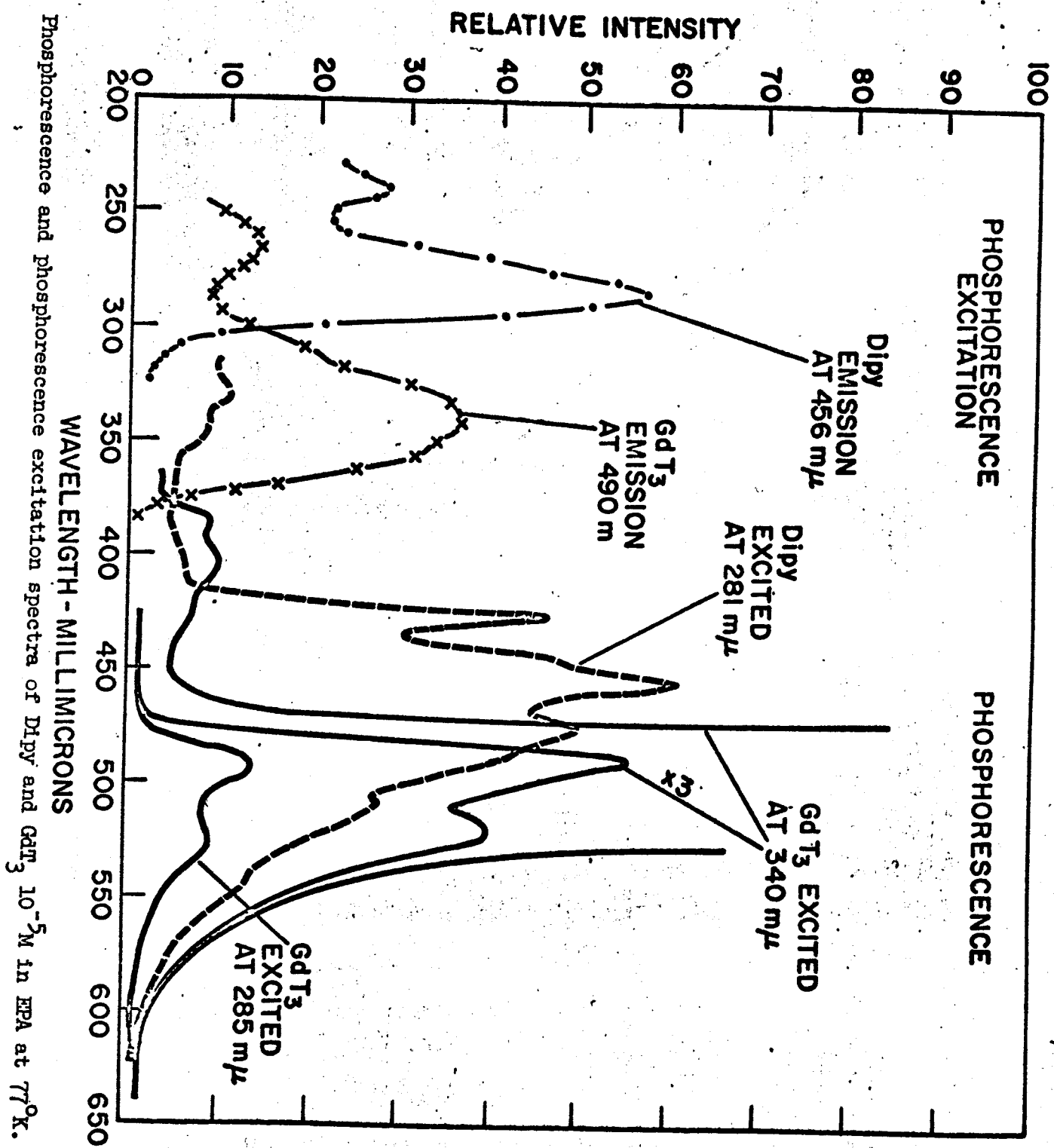


Figure 2. Phosphorescence and phosphorescence excitation spectra of Dipyr and Gd T₃ 10⁻⁵M in EEA at 77°K.

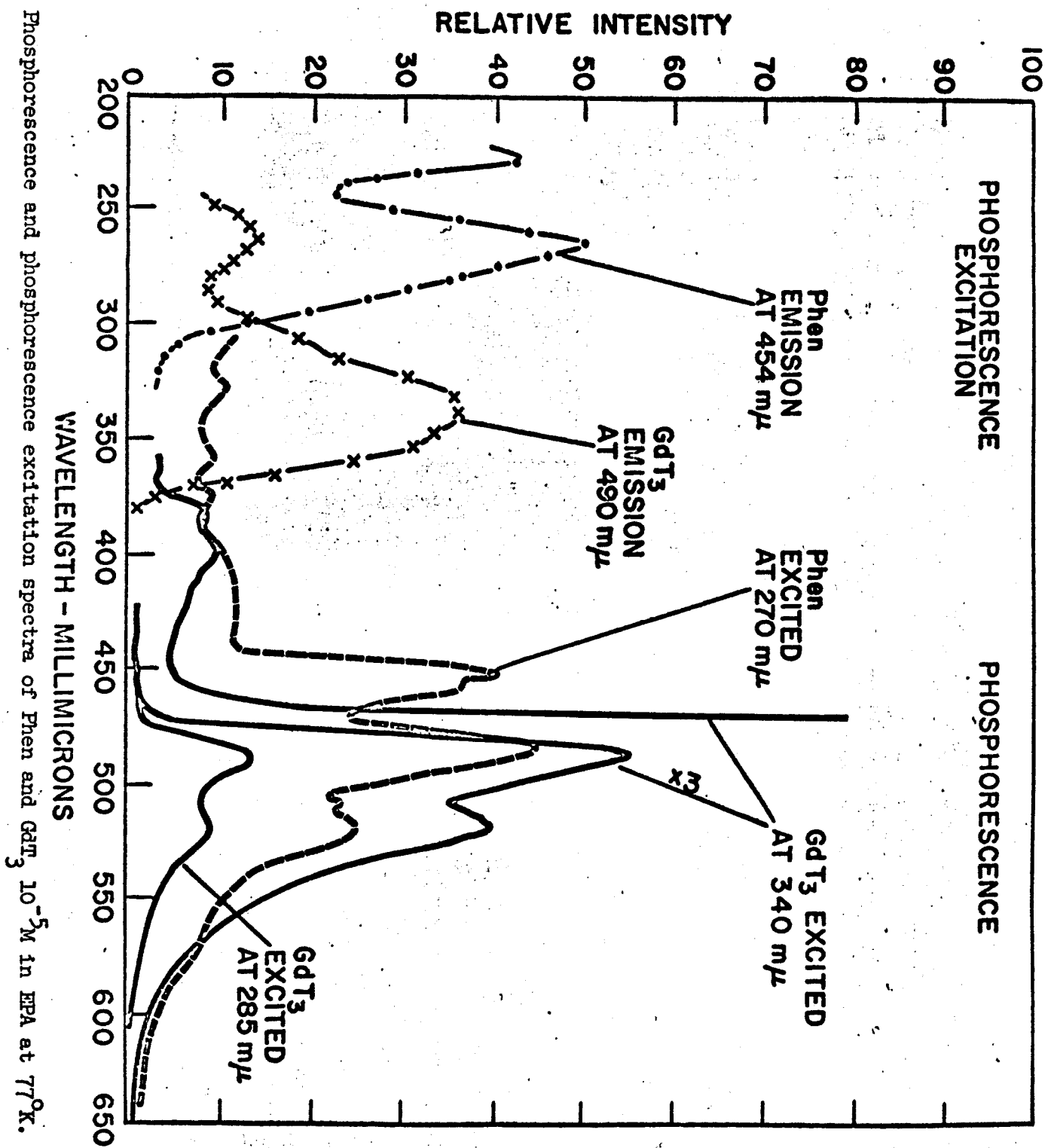


Figure 3. Phosphorescence and phosphorescence excitation spectra of Phen and GdT₃ 10⁻⁵M in EPA at 77°K.

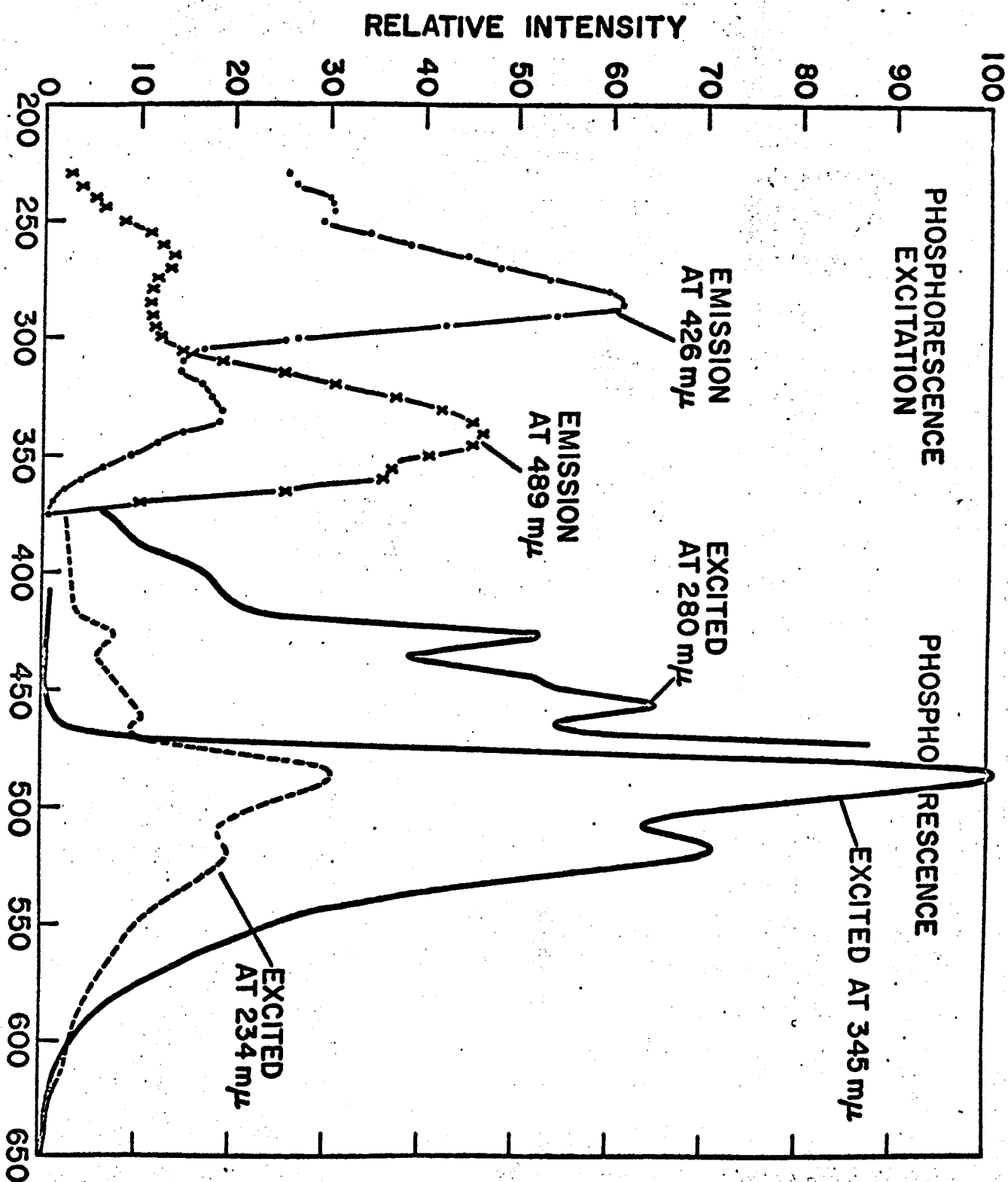


Figure 4. Phosphorescence and phosphorescence excitation spectra of GaTgDipy 10^{-5}M in EPA at 77°K .

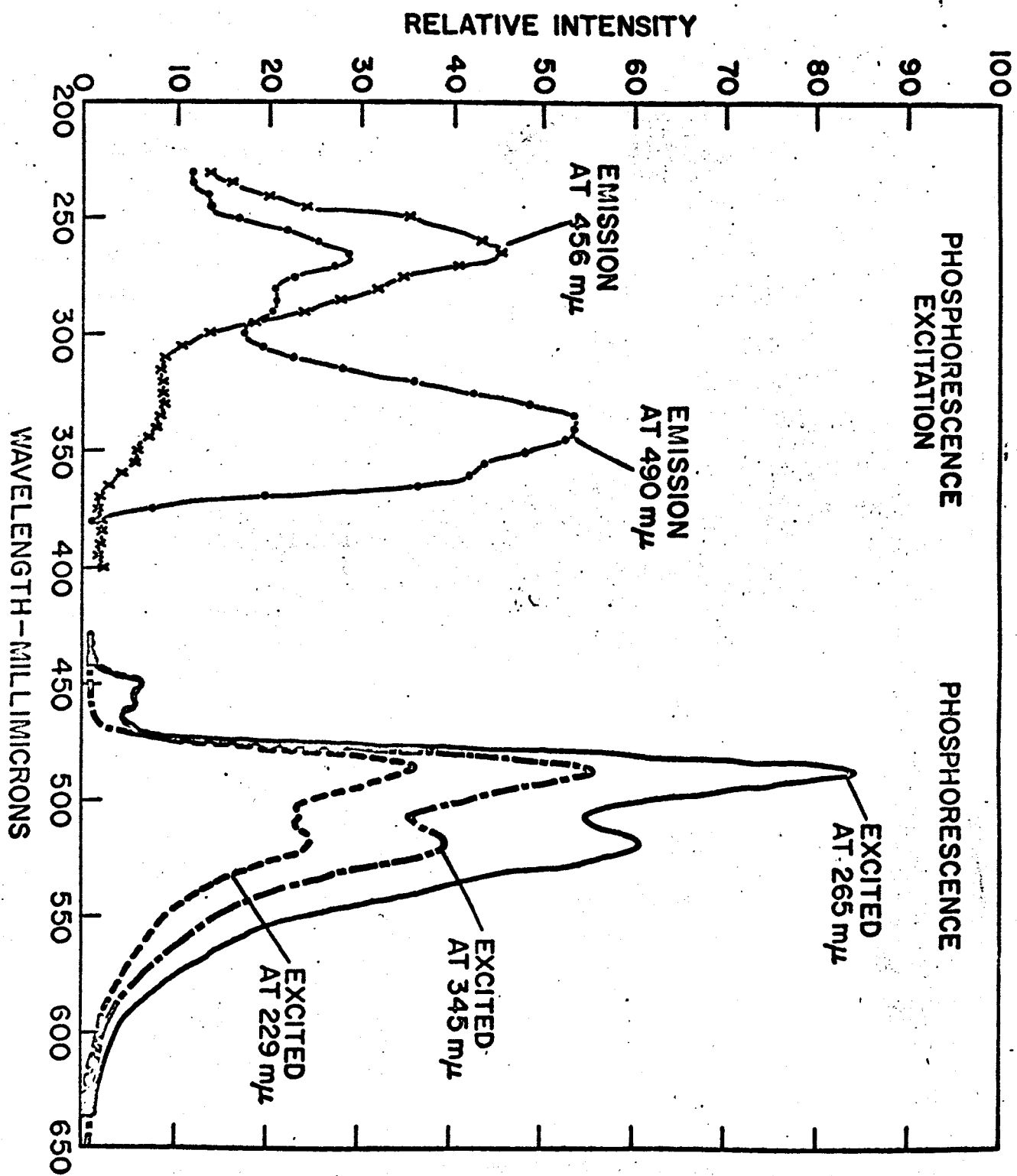
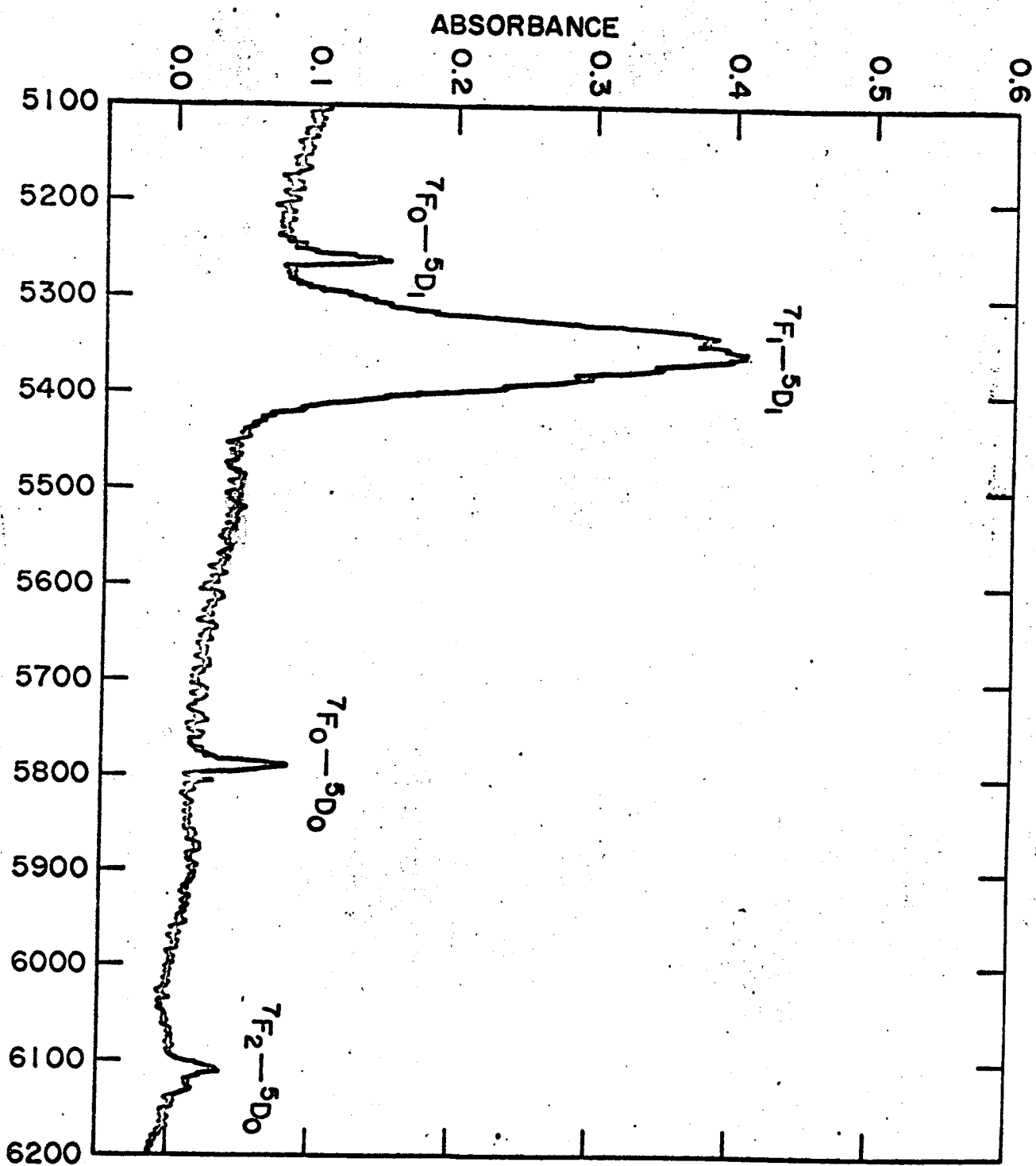


Figure 5. Phosphorescence and phosphorescence excitation spectra of $\text{GdCl}_3 \cdot 7\text{H}_2\text{O}$ in EPA at 77°K .

Figure 6. Absorption spectrum of EuTl_3 10^{-4}M in DMF, 10 cm. path, 298°K .



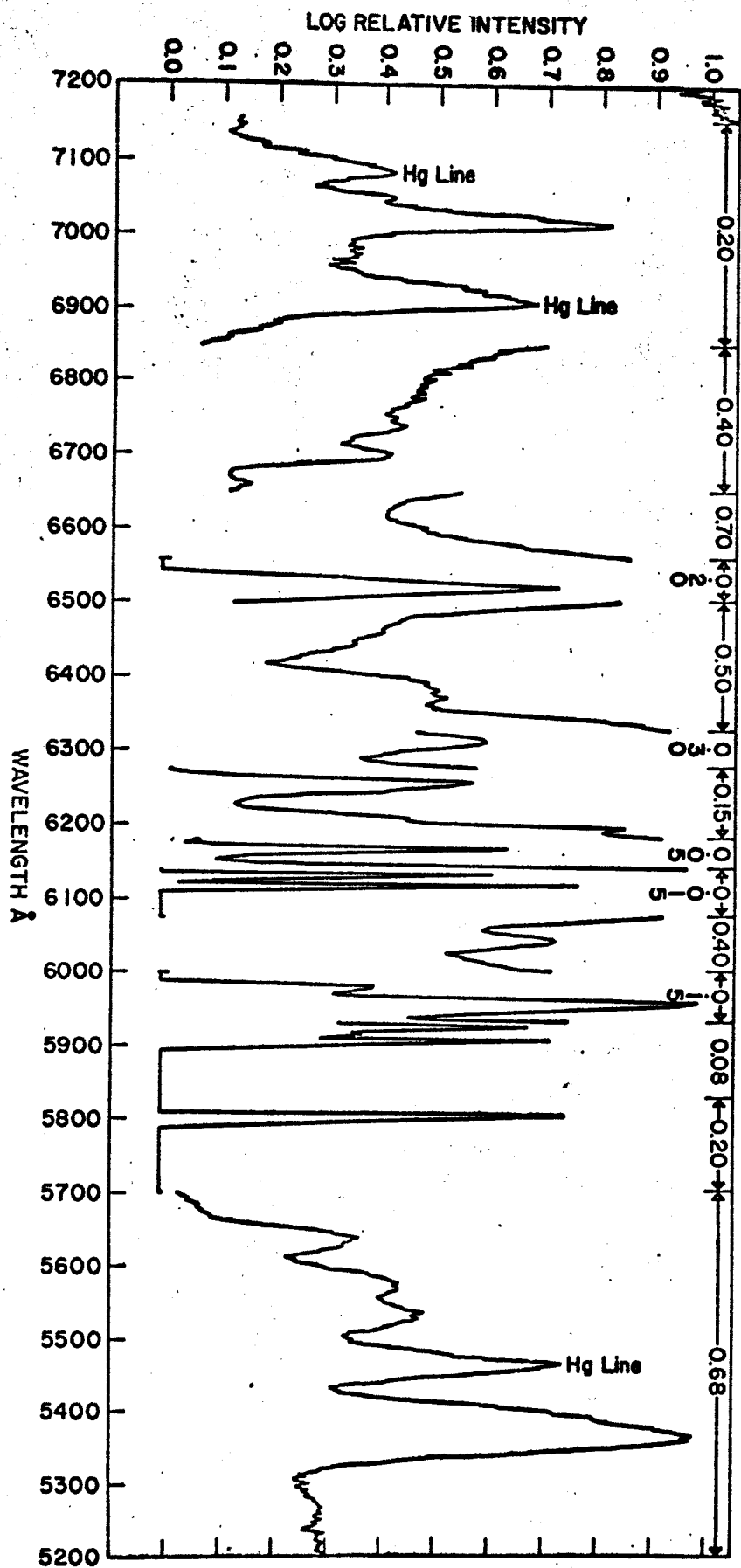


Figure 7. Fluorescence spectrum of microcrystalline EuD_4P at 77°K . (Numbers at the top represent slit-width in mm.)

Figure 8. Fluorescence spectrum of microcrystalline BuF₃ at 77°K.

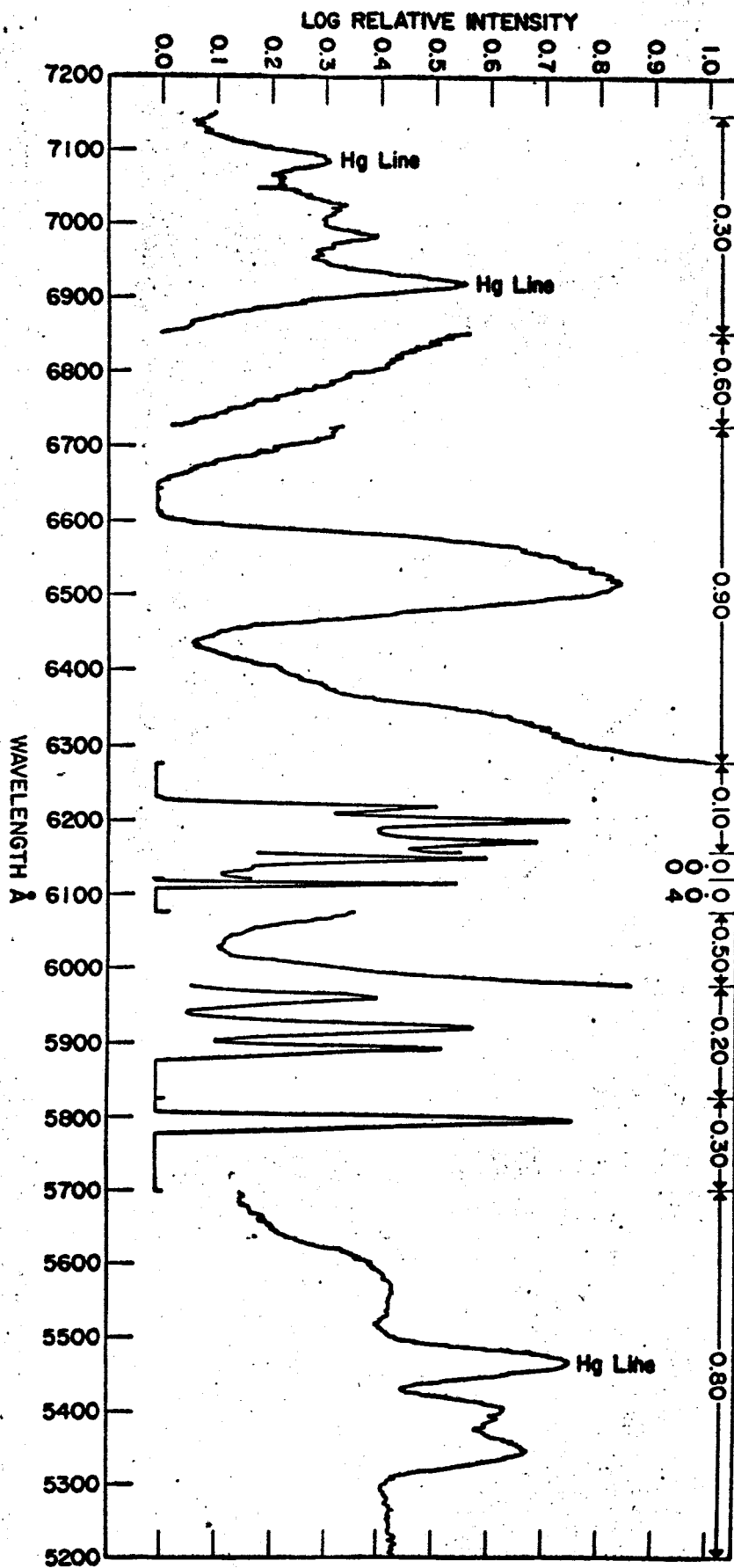


Figure 9. Fluorescence spectrum of microcrystalline Bu₃Dip at 77°K.

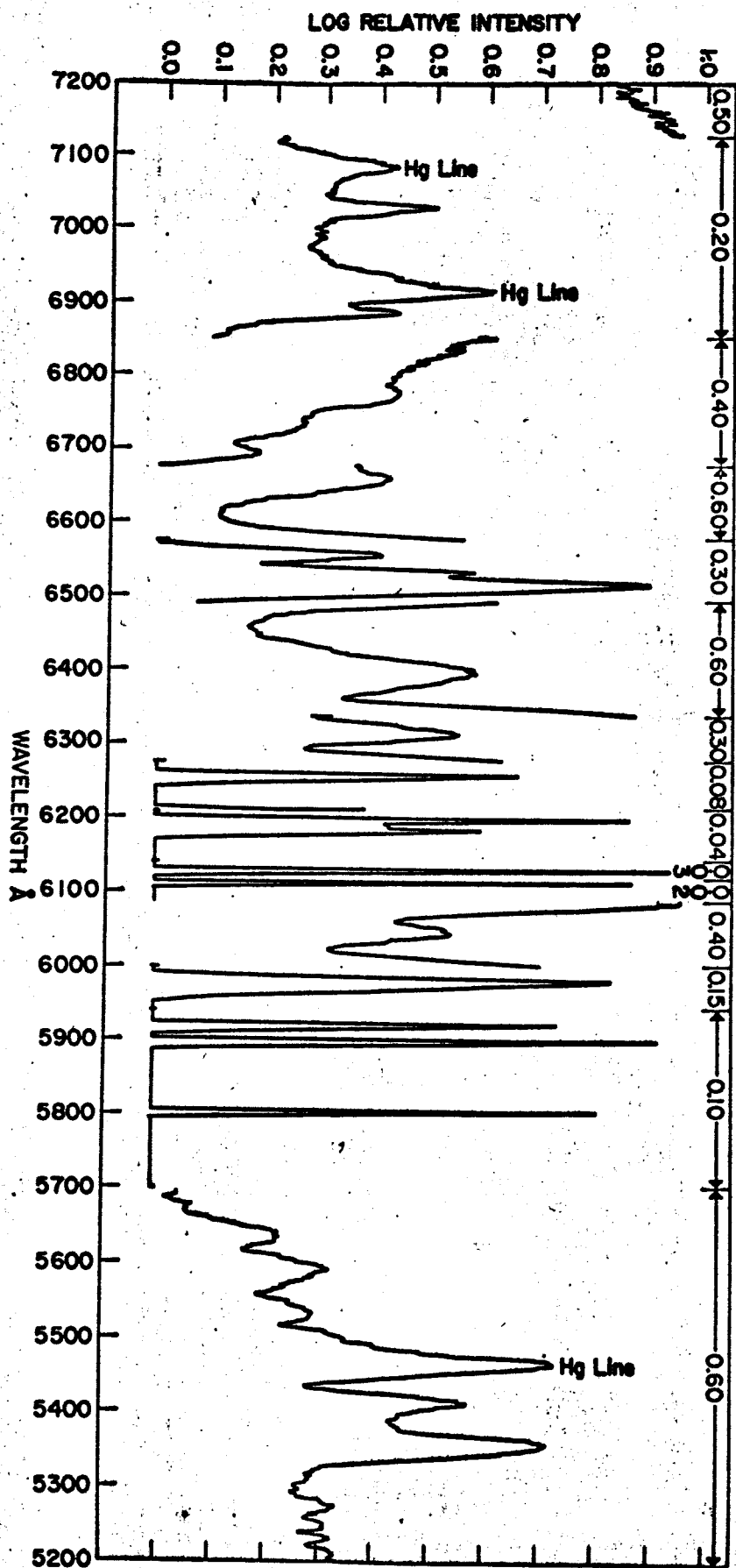


Figure 10. Fluorescence spectrum of microcrystalline Eudipy at 77°K.

